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TITLE: PHOSPHOR COMPRISING OXYNITRIDE GLASS AS MATRIX  
MATERIAL

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ABSTRACT:

**PROBLEM TO BE SOLVED:** To provide a phosphor suitable for a visible illuminant, including a white LED phosphor which uses blue LED as an illuminant, and conventionally, an oxide series phosphor has generally over 400 nm and greatly decreases excitation spectrum intensity, and in white LED coated an InGaN series blue LED(light emission diode) ship with a YAG series fluophor, an excitation peak of the fluophor does not effectively lap on a light emission peak of the blue LED and locates in a short wavelength side, resultingly, in a white LED manufacture with high luminance, the phosphor has not good excitation efficiency.

**SOLUTION:** The phosphor comprising an oxynitride glass matrix comprises CaCO<sub>3</sub> of 20-50 mol% (in terms of CaO), Al<sub>2</sub>O<sub>3</sub> of 0-30 mol%, SiO<sub>2</sub> of 25-60 mol%, AlN of 5-50 mol%, and a rare earth oxide or a transition metallic oxide of 0.1-20 mol% (the sum of the five components is 100 mol%). A content of nitrogen is

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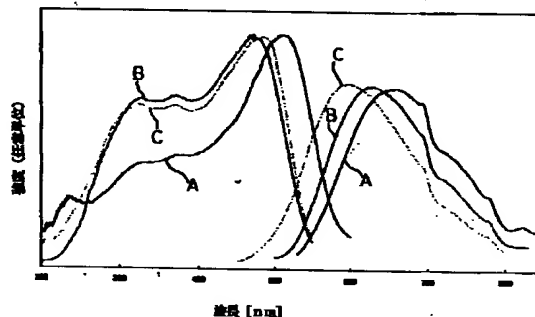
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(54) 【発明の名称】 オキシ窒化物ガラスを母体材料とした蛍光体

(57) 【要約】 (修正有)

【課題】 酸化物系蛍光体は一般に波長400nm超で励起スペクトル強度が著しく減少し、InGa<sub>N</sub>系青色LED(発光ダイオード)チップにYAG系蛍光体を塗布した白色LEDでは蛍光体の励起ピークが青色LEDの発光ピークと効率よく重ならず短波長側に位置するので、高輝度白色LED作製に励起効率のよい蛍光体ではなかった。青色LEDを光源とする白色LEDの蛍光体をはじめ可視光光源に適する蛍光体を提供する。

【構成】 CaCO<sub>3</sub>(CaO換算):20~50モル%、Al<sub>2</sub>O<sub>3</sub>:0~30モル%、SiO<sub>2</sub>:25~60モル%、AlN:5~50モル%、希土類酸化物または遷移金属酸化物:0.1~20モル%(5成分計100モル%)となるオキシナイトライドガラス母体の蛍光体。窒素含有量は15wt%以下とする。他の希土類元素イオン0.1~10モル%(酸化物換算)を蛍光ガラス中に共賦活剤として含んでもよい。



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## 【特許請求の範囲】

【請求項1】 モル%表示で、 $\text{CaCO}_3$ を $\text{CaO}$ に換算して：20～50モル%、 $\text{Al}_2\text{O}_3$ ：0～30モル%、 $\text{SiO}_2$ ：25～60モル%、 $\text{AlN}$ ：5～50モル%、希土類酸化物または遷移金属酸化物：0.1～20モル%で、5成分の合計が100モル%となるオキシ窒化物ガラスを母体材料とした蛍光体。

【請求項2】 窒素含有量が15wt%以下であることを特徴とする請求項1記載のオキシ窒化物ガラスを母体材料とした蛍光体。

【請求項3】 請求項1記載の希土類酸化物イオンの他に増感剤となる他の希土類元素イオンを希土類酸化物として蛍光ガラス中に0.1～10モル%の含有量で共賦活剤として含むことを特徴とする請求項1記載のオキシ窒化物ガラスを母体材料とした蛍光体。

【請求項4】  $\text{InGaN}$ 系青色発光ダイオードを光源とし、請求項1乃至3のいずれか一つに記載された蛍光体を用いたことを特徴とする白色発光ダイオード。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、蛍光体、特に青色発光ダイオード（青色LED）を光源とする白色発光ダイオード（白色LED）の蛍光体として有用な蛍光体に関する。

## 【0002】

【従来の技術】希土類元素を使用した粉末や薄膜状の酸化物蛍光体は従来から広く知られてきたが、一方で、非酸化物に希土類元素を賦活した蛍光体の研究例は少なく、例えば、窒化物やオキシ窒化物については、 $\beta$ サイアロン構造などの $\text{Si-O-N}$ 系のオキシ窒化物結晶（特開昭60-206889号公報、J.W.H. van Krevel et al [Long wavelength  $\text{Ce}^{3+}$  emission in Y-Si-O-N materials], Journal of Alloys and Compounds 268 (1998) 272-277）などが開示されているにすぎない。

【0003】また、結晶性の粉末や薄膜ではなく、ガラス状態にある蛍光体としては発光中心である $\text{Eu}_2\text{O}_3$ や $\text{Tb}_2\text{O}_3$ を比較的多量に含有するフッ燐酸塩蛍光ガラス（特開平8-133780号公報）や酸化物蛍光ガラス（特開平10-167755号公報）が知られている。

【0004】従来、照明機器産業・ディスプレイ産業の①防災照明など信頼性を要求される分野、②車載照明や液晶バックライトなど小型・軽量が好まれる分野、③駅の行き先案内板など視認性を必要とする分野で白色LEDが使用されている。白色LEDの発光色は光の混色に関する原理によって得られるものであり、蛍光体に吸収された青色光は励起源としても働き、黄色の蛍光を発する。この黄色光と青色光が混ぜ合わされて人間の目には白色として見える。

【0005】白色LEDに適する蛍光体として、特に、

$(\text{Y, Gd})_3(\text{Al, Ga})_5\text{O}_{12}$ の組成式で表されるYAG系酸化物母体格子中にCeをドープした蛍光体が知られている。この蛍光体は従来から発光源の $\text{InGaN}$ 系青色LEDチップ表面に薄くコーティングして用いられている。

【0006】しかし、白色LEDの光源として利用される $\text{InGaN}$ 系青色LEDの示す発光ピークは465～520nmで、YAG系蛍光体を励起することができる波長範囲より長波長側に位置する。

## 10 【0007】

【発明が解決しようとする課題】従来の酸化物系蛍光体は、波長400nmを超えると励起スペクトル強度が著しく減少するものが一般的である。このため、 $\text{InGaN}$ 系青色LEDチップにYAG系蛍光体を塗布して作られる白色LED（白色発光ダイオード）では、蛍光体の励起ピークが青色LEDの発光ピークと効率よく重ならず、より短波長側に位置することから、高輝度の白色LEDを作製するのに必ずしも励起効率がよい蛍光体ではなかった。

## 20 【0008】

【課題を解決するための手段】そこで、本発明者は、酸素（-2価）の一部を窒素（-3価）に置き換え、結合のイオン性や共有性の割合が変われば励起・発光波長が自在に変化するとに着想に至り、全体の電荷を中性にバランスさせたガラス系においてアルカリ土類（+2価）と発光中心イオンとを加えて本発明を完成させた。こうした発想は新規であり、可視・紫外光領域の広い波長範囲（ $\leq 550\text{nm}$ ）に励起スペクトルをもったオキシ窒化物ガラスの作製は例がない。すなわち、本発明の蛍光体は、オキシ窒化物ガラスを母体材料として用い、母体材料の $\text{Ca}^{2+}$ イオンの一部を発光中心となる $\text{Eu}^{2+}$ 、 $\text{Eu}^{3+}$ 、 $\text{Ce}^{3+}$ 、 $\text{Tb}^{3+}$ などの希土類イオンまたは $\text{Cr}^{3+}$ 、 $\text{Mn}^{2+}$ などの遷移金属イオンで置換して合成したものである。

## 30

【0009】本発明は、モル%表示で、 $\text{CaCO}_3$ を $\text{CaO}$ に換算して：20～50モル%、 $\text{Al}_2\text{O}_3$ ：0～30モル%、 $\text{SiO}_2$ ：25～60モル%、 $\text{AlN}$ ：5～50モル%、希土類酸化物または遷移金属酸化物：0.1～20モル%で、5成分の合計が100モル%となるオキシ窒化物ガラスを母体材料とした蛍光体である。

## 40

【0010】また、本発明は、窒素含有量が15wt%以下であることを特徴とする上記のオキシ窒化物ガラスを母体材料とした蛍光体である。

【0011】また、本発明は、前記の希土類酸化物イオンの他に増感剤となる他の希土類元素イオンを希土類酸化物として蛍光ガラス中に0.1～10モル%の範囲の含有量で共賦活剤として含むことを特徴とする上記のオキシ窒化物ガラスを母体材料とした蛍光体である。

【0012】さらに、本発明は、 $\text{InGaN}$ 系青色LEDを光源とする上記の蛍光体を用いた白色LEDであ

る。

【0013】本発明の蛍光体の成分の $\text{CaCO}_3$ は、 $\text{CaO}$ の原料であり、ガラス化範囲を広げるだけでなく、蛍光ガラス中に発光中心となる希土類イオンまたは遷移金属イオンを多量に、かつ、安定に含有させることができる。20～30モル%の範囲がより好ましい。なお、 $\text{Ca}^{2+}$ サイトにある $\text{Ca}^{2+}$ イオンを $\text{Sr}^{2+}$ や $\text{Ba}^{2+}$ イオンに容易に置き換えることによって発光中心イオンとなる希土類酸化物または遷移金属酸化物の含有量を上記のとおり0.1～20モル%の範囲内で自在に制御することが可能になる。

【0014】 $\text{AlN}$ と $\text{Al}_2\text{O}_3$ は、窒素含有量を変化させるために用いる。 $\text{AlN}$ が40～10モル%、 $\text{Al}_2\text{O}_3$ が0～20モル%の範囲がより好ましい。 $\text{SiO}_2$ は、ガラス形成成分の一つであり、 $\text{CaO}$ と組み合わせることによりガラス融液の熔融温度を低下させる。30～40モル%の範囲がより好ましい。

【0015】希土類酸化物または遷移金属酸化物は、 $\text{Eu}^{2+}$ 、 $\text{Eu}^{3+}$ 、 $\text{Ce}^{3+}$ 、 $\text{Tb}^{3+}$ などの希土類イオンまたは $\text{Cr}^{3+}$ 、 $\text{Mn}^{2+}$ などの遷移金属イオンをガラス中にドーピングする原料であり、ガラス組成限界である20モル%以下の範囲において賦活し、発光中心の濃度消光が認められない0.5～10モル%の賦活量において強い発光強度を有する。

【0016】オキシ窒化物ガラスは、酸素の一部を窒素に置換したものであり、窒素の導入によってガラス網目構造の化学結合が強化され、ガラス転移温度、軟化温度などの熱的性質の他、機械的な性質や化学的な性質が著しく向上する（例えば、特公平7-37333号公報）ことが知られている。

【0017】本発明の蛍光体は、ガラス中の窒素含有量は、15wt%以下のガラス組成範囲において窒素含有量を制御して発光スペクトルのピーク位置を移動させることができ、さらにオキシ窒化物ガラス蛍光体の励起スペクトル中のピーク波長を紫外から緑の範囲で調整できる。この発光ピーク波長の移動はゆるやかに黄から赤に変化するため、窒素含有量を変化させることにより蛍光体の多色化が容易に図れる。より好ましい窒素含有量は、4～7wt%である。

【0018】オキシ窒化物ガラスを製造する代表的な方法としては二つの方法があり、一つは窒素源に窒化物を用いて熔融する方法であり、他の方法としてはゾルゲル法などで作製した多孔質ガラスをアンモニアガスで窒化させる方法がある。

【0019】前者の方法は熔融時の高温で窒化物が分解するので、窒素含有量を10wt%以上にすることは非常に難しいが、例えば、10気圧の窒素加圧下でこれらのガラスを合成することにより、比較的多量の窒素を含むオキシ窒化物ガラスが得られる。このようなオキシ窒化物ガラスは、機械的強度や化学的安定性にさらに優れ

る

【0020】蛍光ガラス中には、基本的に一種類の発光中心しか含まない。ただし、二種類の希土類元素が蛍光ガラス中に含まれる場合は有り得る。この二種類を同時に蛍光ガラスにドーピングする効果として二つ挙げることができる。一つは、増感作用、もう一つは、キャリアのトラップ準位を新たに形成し、長残光性の発現および改善やサーモルミネッセンスを改善させるというものである。増感作用が観察される組み合わせとして、一般的に、 $\text{Eu}^{3+}$ イオンに対して $\text{Tb}^{3+}$ イオン、 $\text{Tb}^{3+}$ イオンに対して $\text{Ce}^{3+}$ イオンが挙げられる。

【0021】 $\text{Eu}^{2+}$ （あるいは $\text{Ce}^{3+}$ ）イオンのほかに他の希土類元素イオン（ $\text{Gd}^{3+}$ 、 $\text{Tb}^{3+}$ 、 $\text{Dy}^{3+}$ 、または $\text{Sm}^{3+}$ イオンなど）を増感剤とするために、これら希土類酸化物を蛍光ガラス中に0.1～10モル%の含有量で共賦活剤として含ませることができる。

【0022】オキシ窒化物ガラスとしては、 $\text{Si-O-N}$ 、 $\text{Mg-Si-O-N}$ 、 $\text{Al-Si-O-N}$ 、 $\text{Nd-Al-Si-O-N}$ 、 $\text{Y-Al-Si-O-N}$ 、 $\text{Ca-Al-Si-O-N}$ 、 $\text{Mg-Al-Si-O-N}$ 、 $\text{Na-Si-O-N}$ 、 $\text{Na-Ca-Si-O-N}$ 、 $\text{Li-Ca-Al-Si-O-N}$ 、 $\text{Na-B-Si-O-N}$ 、 $\text{Na-Ba-B-Al-Si-O-N}$ 、 $\text{Ba-Al-Si-O-N}$ 、 $\text{Na-B-O-N}$ 、 $\text{Li-P-O-N}$ 、 $\text{Na-P-O-N}$ などの系が知られている。

【0023】これらの系の中で、本発明の母材となる系は、 $\text{Ca-Al-Si-O-N}$ 系オキシ窒化物ガラス（作花らが1983年に作製したもの。[Journal of Non-Crystalline Solids 56(1983)147-152]）に相当する組成を有する。

【0024】この $\text{Ca-Al-Si-O-N}$ 系オキシ窒化物ガラスの窒素含有量は、約5.5wt%と報告されており、本発明の蛍光体の母材ガラスとしてこのオキシ窒化物ガラスの組成を用いることができる。

【0025】本発明の $\text{Ca-Al-Si-O-N}$ 系オキシ窒化物ガラス蛍光体の製造方法は上述の従来公知の方法を用いることができるが、その場合、希土類酸化物を原料として用い、他の原料と混合し、これを出発原料として窒素雰囲気において加熱熔融して蛍光ガラスを合成する。

【0026】例えば、希土類酸化物、金属酸化物 $\text{CaO}$ （← $\text{CaCO}_3$ 、 $\text{Al}_2\text{O}_3$ 、 $\text{SiO}_2$ ）に $\text{AlN}$ を加え、高温、例えば1700℃程度で融解して合成することができる。この際に、 $\text{Al}_2\text{O}_3$ と $\text{AlN}$ の割合を変えることによって、ガラスにおける窒素含有量を変化させることができる。

【0027】以下に、 $\text{Eu}^{2+}$ イオンをドーピングした $\text{Ca-Al-Si-O-N}$ 系オキシ窒化物ガラスにおける窒素含有量と励起・発光スペクトルとの関係を詳しく説明する。試料の調製は下記の原料組成を用いて行った。原料

粉末を以下の試料A、B、Cの各組成で混合し、この混合試料粉末を炉材との反応を避けるためにモリブデン箔に包み、高周波炉を用いて、窒素雰囲気下、1700℃において2時間、加熱溶融し、さらに急冷して蛍光ガラスを得た。

【0028】(試料A)

$\text{CaCO}_3 : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{AlN} : \text{Eu}_2\text{O}_3 = 24.0 : 3.3 : 33.4 : 33.3 : 6.0$   
(N: 5wt%)

(試料B)

$\text{CaCO}_3 : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{AlN} : \text{Eu}_2\text{O}_3 = 26.2 : 9.1 : 36.4 : 21.8 : 6.5$   
(N: 3wt%)

(試料C)

$\text{CaCO}_3 : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{AlN} : \text{Eu}_2\text{O}_3 = 27.7 : 15.4 : 38.5 : 11.5 : 6.9$   
(N: 2wt%)

【0029】図1に、 $\text{Eu}^{2+}$ イオンをドーブしたCa-Al-Si-O-N系オキシ窒化物ガラスの励起・蛍光スペクトルを示す。蛍光ガラスの窒素含有量は、試料Aから試料Cになるにしたがい減少する。これらの蛍光体の励起スペクトル強度は、400nmから急に増加し、500nm辺りに最大値を持つ。一方、発光スペクトルのピークは、600nm辺り(赤色)となった。発光スペクトルの位置は、ガラス中の窒素含有量が減少すると短波長側にシフトした。このように、窒素含有量をコントロールすることにより、蛍光体の多色化が可能である。試料Aは、約5wt%の窒素含有量を有し、試料Bは、約3wt%の窒素含有量を有し、試料Cは、約2wt%の窒素含有量を有する。

【0030】図1の励起スペクトルには二つのピークを有する。250~350nmのピークはEu-Oの電荷移動吸収帯に、一方、450~550nmのピークはEu-Nの電荷移動吸収帯にそれぞれ帰属される。したがって、蛍光ガラス中の窒素含有量が減少すれば450~550nmのEu-Oの電荷移動吸収帯ピークが減少する。

【0031】本発明のオキシ窒化物ガラス蛍光体は、InGa系青色LEDを励起光(450~550nm)とする場合、窒素含有量が大きいほどよいと言える。試料Aと試料Bとを比較すると、窒素含有量の増加に伴いEu-Nの電荷移動吸収帯のピークは長波長側に移動することが分かる。よって、窒素含有量を僅かに変化させることにより、各種の青色LEDの励起光の波長に一致させることができる。

【0032】試料Aから試料Cに窒素含有量を減少させると、680nmから580nmへと発光ピークが連続的に移動する。励起スペクトルのピーク位置を材料設計に取り入れないとすると、窒素含有量をコントロールすることで580~680nmまでの発光を有する蛍光ガ

ラスを得ることができる。

【0033】以上の結果より、窒素含有量は、4~7wt%がよく、この範囲において窒素含有量を変化させることにより必要に応じた励起・発光スペクトルを持つ蛍光ガラスを合成することができる。

【0034】

【実施例】実施例1

$\text{Eu}^{2+}$ イオンをドーブした実施例

原料粉末を以下の組成で混合し、この混合試料粉末をモリブデン箔に包み、高周波加熱炉を用いて、窒素雰囲気下、1700℃において2時間、加熱溶融し、さらに急冷して蛍光ガラスを得た。

【0035】(試料A)

$\text{CaCO}_3 : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{AlN} : \text{Eu}_2\text{O}_3 = 28.2 : 3.1 : 31.4 : 31.3 : 6.0$   
(N: 5wt%) (Eu: 12.0%)

(試料B)

$\text{CaCO}_3 : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{AlN} : \text{Eu}_2\text{O}_3 = 28.6 : 3.1 : 31.9 : 31.8 : 4.6$   
(N: 5wt%) (Eu: 9.2%)

(試料C)

$\text{CaCO}_3 : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{AlN} : \text{Eu}_2\text{O}_3 = 29.1 : 3.2 : 32.3 : 32.3 : 3.1$   
(N: 5wt%) (Eu: 6.2%)

(試料D)

$\text{CaCO}_3 : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{AlN} : \text{Eu}_2\text{O}_3 = 29.4 : 3.2 : 32.7 : 32.6 : 2.1$   
(N: 5wt%) (Eu: 4.2%)

【0036】図2に、 $\text{Eu}^{2+}$ イオンのドーブ量の異なるCa-Al-Si-O-N系オキシ窒化物ガラスの励起・発光スペクトルを示す。励起・発光スペクトルの形状は、 $\text{Eu}^{2+}$ イオンのドーブ量に関係なく同じである。ただし、励起・発光ピークがDからAへと蛍光ガラス中の $\text{Eu}^{2+}$ イオンの量が増加するとともに長波長側に移動する。

【0037】実施例2

$\text{Ce}^{3+}$ イオンをドーブした実施例

原料粉末を以下の組成で混合し、この混合試料粉末をモリブデン箔に包み、高周波炉を用いて、窒素雰囲気下、1700℃において2時間、加熱溶融し、さらに急冷して蛍光ガラスを得た。

【0038】(試料A)

$\text{CaCO}_3 : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{AlN} : \text{CeO}_2 = 28.3 : 3.3 : 33.8 : 33.6 : 1.0$   
(N: 5wt%) (Ce: 1.0%)

(試料B)

$\text{CaCO}_3 : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{AlN} : \text{CeO}_2 = 29.5 : 3.3 : 33.4 : 33.3 : 0.5$   
(N: 5wt%) (Ce: 0.5%)

【0039】図3に、 $\text{Ce}^{3+}$ イオンをドーブしたCa-

Al-Si-O-N系オキシ窒化物の励起・発光スペクトルを示す。励起スペクトルは、Ce<sup>3+</sup>イオンのドーパ量の変化に伴いその形状を大きく変化させたが、発光スペクトルはあまり変わらず、400~450nmの範囲に最大値を持つブロードなピークを示している。Ce<sup>3+</sup>イオンのドーパ量が少ない試料Bの励起スペクトルは、二つのピークを有し、200~330nmのピークがCe<sup>3+</sup>-O、330~400nmのピークがCe<sup>3+</sup>-Nの電荷移動吸収帯にそれぞれ帰属される。この蛍光ガラスは、いずれも励起光である紫外線照射を止めた後でも発光し続ける長残光性を有している。

#### 【0040】実施例3

##### Cr<sup>3+</sup>をドーパした実施例

原料粉末を以下の組成で混合し、この混合試料粉末をモリブデン箔に包み、高周波炉を用いて、窒素雰囲気下、1700℃において2時間、加熱溶融し、さらに急冷して蛍光ガラスを得た。なお、Cr<sup>3+</sup>を賦活した蛍光ガラスについて、得られた試料の均一性をそれぞれ検討するためにそれぞれ二種類作製した。

#### 【0041】(試料A)

CaCO<sub>3</sub> : Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> : AlN : Cr<sub>2</sub>O<sub>3</sub> = 28.3 : 3.3 : 33.8 : 33.6 : 1.0 (N:5wt%) (Cr:2.0%)

#### (試料B)

CaCO<sub>3</sub> : Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> : AlN : Cr<sub>2</sub>O<sub>3</sub> = 28.3 : 3.3 : 33.8 : 33.6 : 1.0 (N:5wt%) (Cr:2.0%)

【0042】図4に、Cr<sup>3+</sup>イオンをドーパしたCa-Al-Si-O-N系オキシ窒化物ガラスの励起・発光スペクトルを示す。図4において、同じバッチから採取したCr<sup>3+</sup>をドーパしたオキシ窒化物ガラスは、二種類の試料(AとB)が確認された。試料Aの励起スペクトルは470nmの発光をモニターしながら測定した結果である。その発光スペクトルは、270nmを励起光として測定したものである。

【0043】一方、試料Bの励起スペクトル1は、440nmの発光をモニターしながら測定したものである。また、Bの発光スペクトル1は、255nmを励起光として測定したもので、また、Bの発光スペクトル2は、335nmを励起光として測定したものである。

【0044】試料Aの励起・発光スペクトルは試料Bの両スペクトルと異なっているが、よく観察すると、それぞれの励起スペクトルには2つのピークがある。また、発光スペクトルのブロードなピークは350~600nmに同様に存在することを考慮すれば両試料は類似している。なお、励起スペクトルの255nmのピークは、蛍光ガラスが有する母体材料の吸収、335nmのピークは、Cr<sup>3+</sup>イオン自身の吸収としてそれぞれ帰属され

る。

#### 【0045】実施例4

##### Mn<sup>2+</sup>をドーパした実施例

原料粉末を以下の組成で混合し、この混合試料粉末をモリブデン箔に包み、高周波加熱炉を用いて、窒素雰囲気下、1700℃において2時間、加熱溶融し、さらに急冷して蛍光ガラスを得た。なお、Mn<sup>2+</sup>を賦活した蛍光ガラスについて、得られた試料の均一性をそれぞれ検討するためにそれぞれ二種類作製した。

#### 【0046】(試料A)

CaCO<sub>3</sub> : Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> : AlN : MnCO<sub>3</sub> = 29.9 : 2.8 : 33.2 : 33.1 : 1.0 (N:5wt%) (Mn:1.0%)

#### (試料B)

CaCO<sub>3</sub> : Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> : AlN : MnCO<sub>3</sub> = 29.9 : 2.8 : 33.2 : 33.1 : 1.0 (N:5wt%) (Mn:1.0%)

【0047】図5に、Mn<sup>2+</sup>イオンをドーパしたCa-Al-Si-O-N系オキシ窒化物ガラスの励起・発光スペクトルを示す。図5における試料Aと試料Bの励起・発光スペクトルの比較から、Mn<sup>2+</sup>をドーパしたオキシ窒化物ガラスは、均一である。

#### 【0048】

【発明の効果】本発明の蛍光体は、励起スペクトルの位置が酸化物ガラスと比較して長波長側に著しく移動し、吸収ピークが青色LEDの発光ピーク近辺(450~520nm)で最大となり、さらに、ピーク幅も大きくなるため、InGaP系青色LEDを励起光源にした場合、この蛍光体と組み合わせると効率よく励起され、より明るい白色LEDが実現できる。また、ガラスはオキシ窒化物のような結晶とは異なり、構造がルーズな分、反応条件さえ満たすことができれば、オキシ窒化物ガラス中のOとNの比を自由に定めることができ、N含有量の変化による蛍光体の多色化が容易に図れる。

#### 【図面の簡単な説明】

【図1】図1は、本発明のEuをドーパしたオキシ窒化物ガラスのN含有量依存性を示す励起・発光スペクトルのグラフである。

【図2】図2は、本発明のEuをドーパしたオキシ窒化物ガラスのEu量依存性を示す励起・発光スペクトルのグラフである。

【図3】図3は、本発明のCeをドーパしたオキシ窒化物ガラスの励起・発光スペクトルのグラフである。

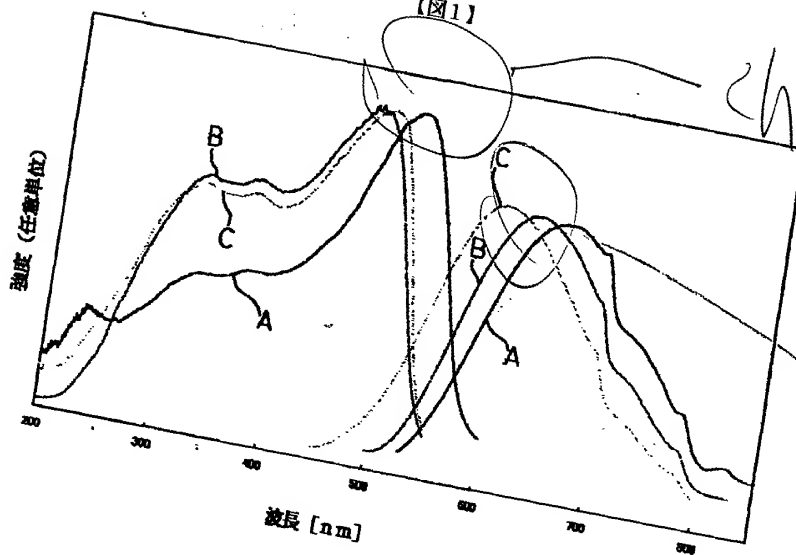
【図4】図4は、本発明のCrをドーパしたオキシ窒化物ガラスの励起・発光スペクトルのグラフである。

【図5】図5は、本発明のMnをドーパしたオキシ窒化物ガラスの励起・発光スペクトルのグラフである。

(6)

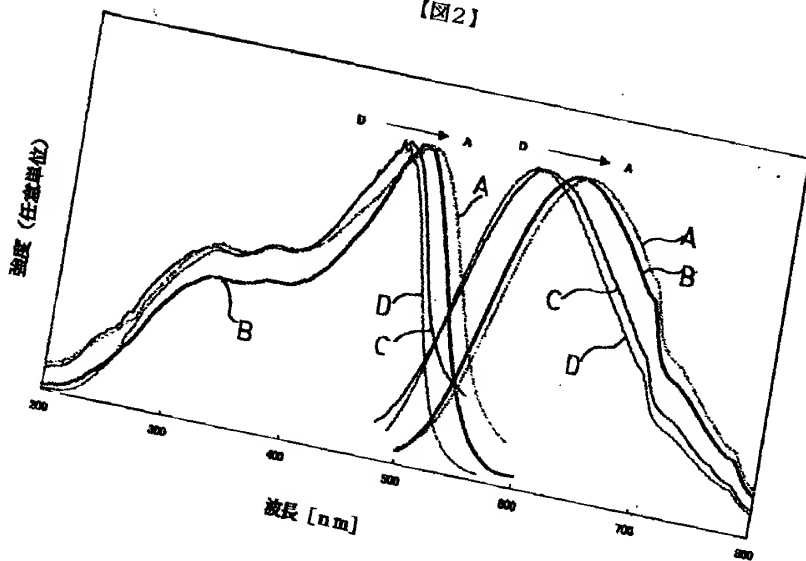
特開2001-214162

【図1】



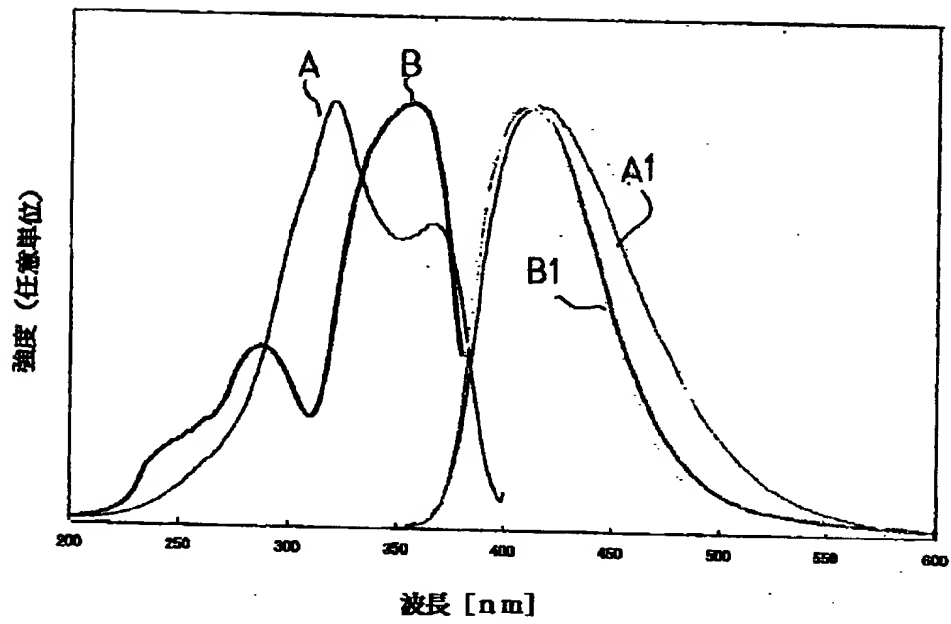
Charge Transfer Absorption  
luminescent Peak

【図2】

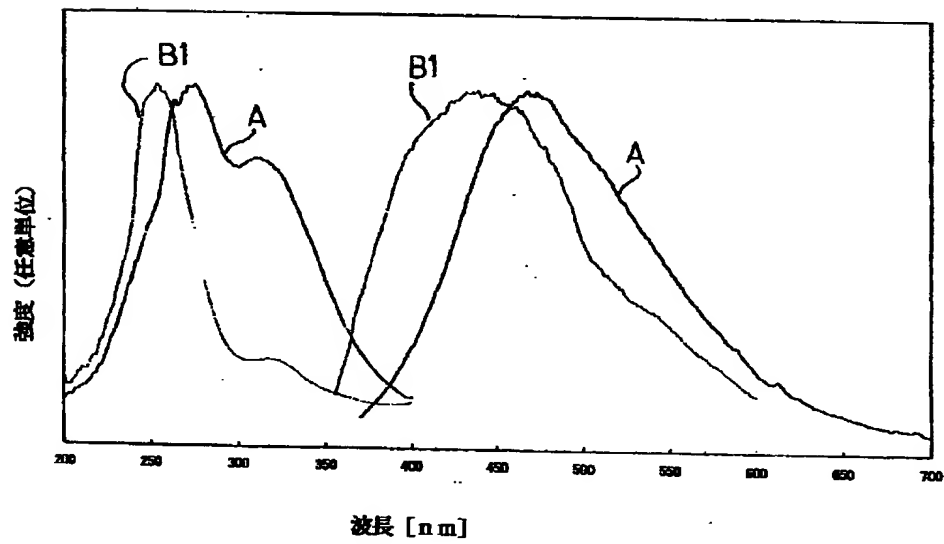




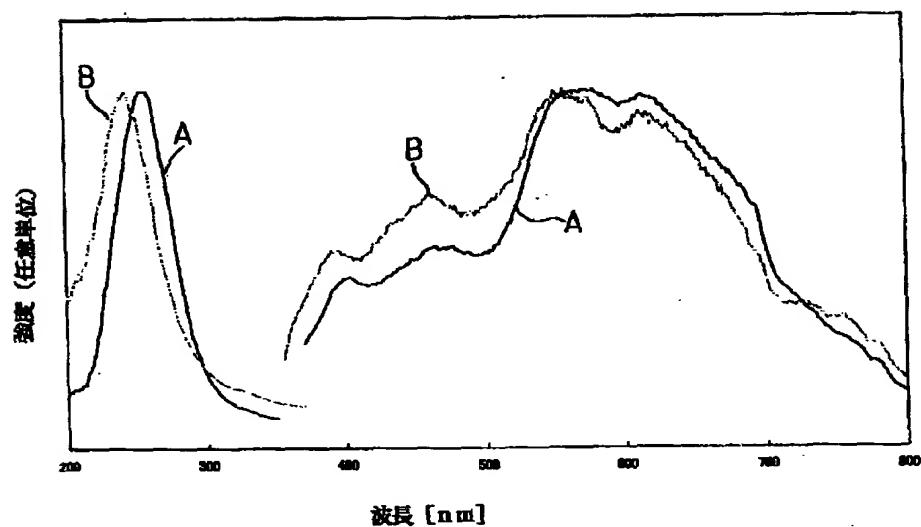
【図3】



【図4】



【図5】



フロントページの続き

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 HH11 HH13 HH15 HH17 HH20  
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 JJ10 KK01 KK03 KK04 KK05  
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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a fluorescent substance, especially a fluorescent substance useful as a fluorescent substance of the white light emitting diode (white Light Emitting Diode) which uses blue light emitting diode (blue Light Emitting Diode) as the light source.

[0002]

[Description of the Prior Art] Although the powder and the thin film-like oxide emitter which used rare earth elements are widely known from the former There are few examples of research of the emitter which carried out activation of the rare earth elements to the non-oxide. on the other hand, about a nitride or an oxy-nitride the oxy-nitride crystal (JP,60-206889,A --) of Si-O-N systems, such as beta sialon structure J. W.H.van Krevel et al "Long wavelength Ce<sup>3+</sup> emission in Y-Si-O-N materials", Journal of Alloys and Compounds 268 272(1998)-277, etc. are indicated.

[0003] Moreover, it is Eu<sub>2</sub>O<sub>3</sub> which is an emission center as an emitter in crystalline vitreous state instead of powder or a thin film. Tb<sub>2</sub>O<sub>3</sub> The FUTSU phosphate fluorescent glass (JP,8-133780,A) and oxide fluorescent glass (JP,10-167755,A) which are contained comparatively so much are known.

[0004] Conventionally, white Light Emitting Diode is used in the field which needs visibility, such as a destination guide plate of small and lightweight \*\*\*\* rare \*\*\*\*\*, such as a field, \*\* mount lighting, the liquid crystal back light, etc. of which reliability, such as \*\* disaster prevention lighting of lighting device industry and display industry, is required, and \*\* station. The luminescent color of white Light Emitting Diode is obtained by the principle about the color mixture of light, and the blue glow absorbed by the fluorescent substance works also as a source of excitation, and emits yellow fluorescence. This yellow light and blue glow mix together, are carried out, and it is visible to human being's eyes as white.

[0005] The fluorescent substance which doped Ce as a fluorescent substance suitable for white Light Emitting Diode in the YAG system oxide parent grid especially expressed with the empirical formula of 3 (Y, Gd) 5 (aluminum, Ga) O<sub>12</sub> is known. From the former, the InGa<sub>N</sub> system blue Light Emitting Diode chip front face of the source of luminescence is thinly coated with this fluorescent substance, and it is used for it.

[0006] However, the luminescence peak which InGa<sub>N</sub> system blue Light Emitting Diode used as the light source of white Light Emitting Diode shows is 465-520nm, and is located in a long wavelength side from the wavelength range which can excite a YAG system fluorescent substance.

[0007]

[Problem(s) to be Solved by the Invention] The conventional oxide system fluorescent substance has that common to which excitation-spectrum intensity decreases remarkably, if the wavelength of 400nm is exceeded. For this reason, in white Light Emitting Diode (white light emitting diode) which applies a YAG system fluorescent substance to an InGaN system blue Light Emitting Diode chip, and is made, an excitation efficiency was not necessarily a good fluorescent substance that the excitation peak of a fluorescent substance produces white Light Emitting Diode of high brightness from not lapping with the luminescence peak of blue Light Emitting Diode efficiently, but being located more in a short wavelength side.

[0008]

[Means for Solving the Problem] Then, this invention person transposed a part of oxygen (-divalent) to nitrogen (-trivalent), when the rate of the ionicity of combination or share nature changed, he resulted in the idea that excitation / luminescence wavelength changes free, he added an alkaline earth (+divalent) and emission center ion in the textile glass yarn which made the whole charge balance neutral, and completed this invention. Such the way of thinking is new and production of the oxy-nitride glass which had an excitation spectrum in the large wavelength range of visible and an ultraviolet radiation field ( $\leq 550\text{nm}$ ) does not have an example. That is, the fluorescent substance of this invention replaces and compounds a part of calcium<sup>2+</sup> ion of parent material with transition-metals ion, such as rare earth ion used as an emission center, such as Eu<sup>2+</sup>, Eu<sup>3+</sup>, Ce<sup>3+</sup>, and Tb<sup>3+</sup>, or Cr<sup>3+</sup>, and Mn<sup>2+</sup>, using oxy-nitride glass as a parent material.

[0009] this invention is a mol % display and is CaCO<sub>3</sub>. It converts into CaO and is :20-50-mol % and aluminum 2O<sub>3</sub>. : It is 0-30-mol % and SiO<sub>2</sub>:25-60-mol % and AlN:5-50-mol % and rare earth oxide or transition-metals oxide:0.1-20-mol %, and is the fluorescent substance with which the sum total of five components made parent material the 100-mol oxy-nitride glass with which it becomes %.

[0010] Moreover, this invention is the fluorescent substance which made parent material the above-mentioned oxy-nitride glass characterized by a nitrogen content being less than [ 15wt% ].

[0011] Moreover, this invention is the fluorescent substance which made parent material the above-mentioned oxy-nitride glass characterized by containing as a coactivator by the content of the 0.1-10-mol range of % in a fluorescent glass by using other rare-earth-elements ion used as the sensitizer other than the aforementioned rare earth oxide ion as a rare earth oxide.

[0012] Furthermore, this invention is white Light Emitting Diode using the above-mentioned fluorescent substance which uses InGaN system blue Light Emitting Diode as the light source.

[0013] CaCO<sub>3</sub> of the component of the fluorescent substance of this invention The rare earth ion or transition-metals ion which is the raw material of CaO and it not only extends the vitrification range, but serves as an emission center into a fluorescent glass can be made to contain so much and stably. The 20-30-mol range of % is more desirable. In addition, it becomes possible by transposing easily the calcium<sup>2+</sup> ion in a calcium<sup>2+</sup> site to Sr<sup>2+</sup> or Ba<sup>2+</sup> ion to control the content of the rare earth oxide used as emission center ion, or a transition-metals oxide by 0.1-20-mol% of within the limits free as above-mentioned.

[0014] AlN and aluminum 2O<sub>3</sub> It uses in order to change a nitrogen content. AlN is 40-10-mol % and aluminum 2O<sub>3</sub>. The 0-20-mol range of % is more desirable. SiO<sub>2</sub> It is one of the glass formation components, and is CaO. The melting temperature of a glass melt is reduced by

combining. The 30-40-mol range of % is more desirable.

[0015] In the range not more than 20 mol % which is the raw material which dopes transition-metals ion, such as rare earth ion, such as  $\text{Eu}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Ce}^{3+}$ , and  $\text{Tb}^{3+}$ , or  $\text{Cr}^{3+}$ , and  $\text{Mn}^{2+}$ , in glass, and is a glass composition limitation, activation of a rare earth oxide or the transition-metals oxide is carried out, and it has strong luminescence intensity in % of the 0.5-10-mol amount of activation concentration quenching of an emission center is not accepted to be.

[0016] Oxy-nitride glass replaces a part of oxygen by nitrogen, the chemical bond of the glass network structure is strengthened by introduction of nitrogen, and what (for example, JP, 7-37333, B) others, a mechanical property, and a chemical property improve remarkably is known. [ thermal properties /, such as a glass transition temperature and a softening temperature, ]

[0017] The nitrogen content in glass controls a nitrogen content in the glass composition range not more than 15wt%, and can move the peak position of an emission spectrum, and further, since the fluorescent substance of this invention is ultraviolet, it can adjust the peak wavelength in the excitation spectrum of an oxy-nitride glass fluorescent substance in the green range. Since movement of this emission peak wavelength changes from yellow to red gently, it can attain multiple color-ization of a fluorescent substance easily by changing a nitrogen content. A more desirable nitrogen content is 4 - 7wt%.

[0018] There are two methods as a typical method of manufacturing oxy-nitride glass, one is the method of using and fusing a nitride to a nitrogen source, and it has a method of nitriding the porous glass produced with the sol-gel method etc. as other methods by ammonia gas.

[0019] Since a nitride decomposes the former method at the elevated temperature at the time of melting, although it is very difficult to carry out a nitrogen content more than 10wt%, the oxy-nitride glass containing comparatively a lot of nitrogen is obtained, for example by compounding these glass under the nitrogen pressurization of ten atmospheric pressure. Such oxy-nitride glass is [0020] which is further excellent in a mechanical strength or chemical stability. In a fluorescent glass, only one kind of emission center is included fundamentally. However, it is possible when two kinds of rare earth elements are contained in a fluorescent glass. Two can be mentioned as this effect that dopes two kinds to a fluorescent glass simultaneously. It is a thing of one forming sensitization, and another newly forming the trap level of a carrier, and making a manifestation and an improvement of high-persistence, and thermostat luminescence improve. Generally as a combination in which sensitization is observed,  $\text{Ce}^{3+}$  ion is mentioned to  $\text{Tb}^{3+}$  ion and  $\text{Tb}^{3+}$  ion to  $\text{Eu}^{3+}$  ion.

[0021] In order to make other rare-earth-elements ion ( $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ , or  $\text{Sm}^{3+}$  ion) into a sensitizer besides  $\text{Eu}^{2+}$  (or  $\text{Ce}^{3+}$ ) ion, these rare earth oxide can be included as a coactivator by 0.1-10-mol % of a content in a fluorescent glass.

[0022] As oxy-nitride glass Si-O-N, Mg-Si-O-N, aluminum-Si-O-N, Nd-aluminum-Si-O-N, Y-aluminum-Si-O-N, calcium-aluminum-Si-O-N, Mg-aluminum-Si-O-N, Na -- Si-O-N, Na-calcium-Si-O-N, Li-calcium-aluminum-Si-O-N, Na-B-Si-O-N, Na-Ba-B-aluminum-Si-O-N,

[0023] by which systems, such as Ba-aluminum-Si-O-N, Na-B-O-N, Li-P-O-N, and Na-P-O-N, are known The system which serves as a base material of this invention in these systems is calcium-aluminum-Si-O-N system oxy-nitride glass (work thing which flowers produced in 1983.). "It has composition equivalent to Journal of Non-Crystalline Solids 56 (1983) 147-152.

[0024] It is reported that the nitrogen content of this calcium-aluminum-Si-O-N system oxy-nitride glass is about 5.5 wt(s)%, and composition of this oxy-nitride glass can be used for it as

base material glass of the fluorescent substance of this invention.

[0025] Although the manufacture method of the calcium-aluminum-Si-O-N system oxy-nitride glass fluorescent substance of this invention can use an above-mentioned conventionally well-known method, it mixes with other raw materials in that case, using a rare earth oxide as a raw material, and it carries out heating fusion in nitrogen-gas-atmosphere mind by making this into a start raw material, and compounds a fluorescent glass.

[0026] For example, AlN can be added to a rare earth oxide and a metallic oxide CaO (<-CaCO<sub>3</sub>], aluminum [ 2O<sub>3</sub> ], and SiO<sub>2</sub>), and it can dissolve and compound at an about elevated temperature, for example, 1700 degrees C. In this case, aluminum 2O<sub>3</sub> The nitrogen content in glass can be changed by changing the rate of AlN.

[0027] Below, the relation of the nitrogen content, and the excitation and the fluorescence spectrum in the calcium-aluminum-Si-O-N system oxy-nitride glass which doped Eu<sup>2+</sup> ion is explained in detail. Manufacture of a sample was performed using the following raw material composition. Raw material powder was mixed by each composition of the following samples A, B, and C, this mixed-sample powder was wrapped in the molybdenum foil, in order to avoid a reaction with internal insulation, heating fusion was carried out for 2 hours, it quenched further, and the fluorescent glass was obtained [ in / the bottom of nitrogen-gas-atmosphere mind, and 1700 degrees C / using a high-frequency furnace ].

[0028] ((A) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub> O<sub>3</sub> :SiO<sub>2</sub> :AlN:Eu<sub>2</sub> O<sub>3</sub> =24.0:3.3:33.4:33.3:6.0(N:5wt%)

((B) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub> O<sub>3</sub> :SiO<sub>2</sub> :AlN:Eu<sub>2</sub> O<sub>3</sub> =26.2:9.1:36.4:21.8:6.5(N:3wt%)

((C) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub> O<sub>3</sub> :SiO<sub>2</sub> :AlN:Eu<sub>2</sub> O<sub>3</sub> =27.7:15.4:38.5:11.5:6.9(N:2wt%)

[0029] Excitation and the fluorescence spectrum of the calcium-aluminum-Si-O-N system oxy-nitride glass which doped Eu<sup>2+</sup> ion to drawing 1 <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000003](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000003)> are shown. The nitrogen content of a fluorescent glass decreases as it becomes Sample C from Sample A. The excitation-spectrum intensity of these fluorescent substances increases from 400nm suddenly, and has maximum around [ 500nm ]. On the other hand, the peak of an emission spectrum became 600nm [ about ] (red). The position of an emission spectrum was shifted to the short wavelength side when the nitrogen content in glass decreased. Thus, multiple-color-izing of a fluorescent substance is possible by controlling a nitrogen content. Sample A has an about 5 wt(s)% nitrogen content, Sample B has an about 3 wt(s)% nitrogen content, and Sample C has an about 2 wt(s)% nitrogen content.

[0030] In the excitation spectrum of drawing 1 <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000003](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000003)>, it has two peaks. A 250-350nm peak belongs to the charge transfer absorption band of Eu-O, and, on the other hand, a 450-550nm peak belongs to the charge transfer absorption band of Eu-N, respectively. Therefore, if the nitrogen content in a fluorescent glass decreases, the charge-

transfer-absorption-band peak of 450-550nm Eu-O will decrease.

[0031] It can be said that the oxy-nitride glass fluorescent substance of this invention is so good that a nitrogen content is large when making InGaN system blue Light Emitting Diode into excitation light (450-550nm). When Sample A is compared with Sample B, it turns out with the increase in a nitrogen content that the peak of the charge transfer absorption band of Eu-N moves to a long wavelength side. Therefore, it can be made in agreement with the wavelength of the excitation light of various kinds of blue Light Emitting Diodes by changing a nitrogen content slightly.

[0032] If a nitrogen content is decreased in Sample C from Sample A, a luminescence peak will move to 580nm continuously from 680nm. Supposing it does not take in the peak position of an excitation spectrum to a materials design, the fluorescent glass which has luminescence to 580-680nm can be obtained in controlling a nitrogen content.

[0033] From the above result, 4 - 7wt% of a nitrogen content is good, and a fluorescent glass with excitation and an emission spectrum as occasion demands can be compounded by changing a nitrogen content in this range.

[0034]

[Example] The example raw material powder which doped example 1Eu<sup>2+</sup> ion was mixed by the following composition, this mixed-sample powder was wrapped in the molybdenum foil, heating fusion was carried out for 2 hours, it quenched further, and the fluorescent glass was obtained [ in / the bottom of nitrogen-gas-atmosphere mind, and 1700 degrees C / using a high-frequency-heating furnace ].

[0035] ((A) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub>O<sub>3</sub> :SiO<sub>2</sub> :AlN:Eu<sub>2</sub>O<sub>3</sub> =28.2:3.1:31.4:31.3:6.0(N:5wt%)(Eu:12.0%)

((B) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub>O<sub>3</sub> :SiO<sub>2</sub> :AlN:Eu<sub>2</sub>O<sub>3</sub> =28.6:3.1:31.9:31.8:4.6(N:5wt%)(Eu:9.2%)

((C) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub>O<sub>3</sub> :SiO<sub>2</sub> :AlN:Eu<sub>2</sub>O<sub>3</sub> =29.1:3.2:32.3:32.3:3.1(N:5wt%)(Eu:6.2%)

((D) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub>O<sub>3</sub> :SiO<sub>2</sub> :AlN:Eu<sub>2</sub>O<sub>3</sub> =29.4:3.2:32.7:32.6:2.1(N:5wt%)(Eu:4.2%)

[0036] Excitation and the emission spectrum of the calcium-aluminum-Si-O-N system oxy-nitride glass with which the amounts of dopes of Eu<sup>2+</sup> ion differ in drawing 2

<http://www4.ipdl.jpo.go.jp/cgi-bin/tran\_web.cgi\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000004> are shown. The configuration of excitation and an

emission spectrum is the same regardless of the amount of dopes of Eu<sup>2+</sup> ion. However, excitation / luminescence peak moves to a long wavelength side, while the amount of the Eu<sup>2+</sup> ion in a fluorescent glass increases from D to A.

[0037] The example raw material powder which doped example 2Ce<sup>3+</sup> ion was mixed by the following composition, this mixed-sample powder was wrapped in the molybdenum foil, heating fusion was carried out for 2 hours, it quenched further, and the fluorescent glass was obtained [ in / the bottom of nitrogen-gas-atmosphere mind, and 1700 degrees C / using a high-frequency furnace ].

[0038] ((A) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub>O<sub>3</sub> :SiO<sub>2</sub> :AlN:CeO<sub>2</sub> =28.3:3.3:33.8:33.6:1.0(N:5wt%)(Ce:1.0%)

((B) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub>O<sub>3</sub> :SiO<sub>2</sub> :AlN:CeO<sub>2</sub> =29.5:3.3:33.4:33.3:0.5(N:5wt%)(Ce:0.5%)

[0039] Excitation and the emission spectrum of the calcium-aluminum-Si-O-N system oxy-nitride which doped Ce<sup>3+</sup> ion to [drawing 3](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000005) <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000005](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000005)> are shown. Although the excitation spectrum changed the configuration a lot with change of the amount of dopes of Ce<sup>3+</sup> ion, an emission spectrum is not much unchanging and the broadcloth peak which has maximum in the range of 400-450nm is shown. The excitation spectrum of the sample B with few amounts of dopes of Ce<sup>3+</sup> ion has two peaks, and the peak whose 200-330nm peaks are Ce<sup>3+</sup>-O and 330-400nm belongs to the charge transfer absorption band of Ce<sup>3+</sup>-N, respectively. Each of this fluorescent glass has the high-persistence which continues emitting light after stopping the UV irradiation which is excitation light.

[0040] The example raw material powder which doped example 3Cr<sup>3+</sup> was mixed by the following composition, this mixed-sample powder was wrapped in the molybdenum foil, heating fusion was carried out for 2 hours, it quenched further, and the fluorescent glass was obtained [ in / the bottom of nitrogen-gas-atmosphere mind, and 1700 degrees C / using a high-frequency furnace ]. In addition, in order to examine the homogeneity of the obtained sample about the fluorescent glass which carried out activation of Cr<sup>3+</sup>, respectively, two kinds were produced, respectively.

[0041] ((A) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub>O<sub>3</sub> :SiO<sub>2</sub> :AlN:Cr<sub>2</sub>O<sub>3</sub> =28.3:3.3:33.8:33.6:1.0(N:5wt%)(Cr:2.0%)

((B) Sample)

CaCO<sub>3</sub> :Al<sub>2</sub>O<sub>3</sub> :SiO<sub>2</sub> :AlN:Cr<sub>2</sub>O<sub>3</sub> =28.3:3.3:33.8:33.6:1.0(N:5wt%)(Cr:2.0%)

[0042] Excitation and the emission spectrum of the calcium-aluminum-Si-O-N system oxy-nitride glass which doped Cr<sup>3+</sup> ion to [drawing 4](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000006) <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000006](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000006)> are shown. In [drawing 4](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000006) <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000006](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000006)> , as for the oxy-nitride glass which doped Cr<sup>3+</sup> extracted from the same batch, two kinds of samples (A and B) were checked. The excitation spectrum of Sample A is the result of measuring acting as the monitor of the 470nm luminescence. The emission spectrum measures 270nm as an excitation light.

[0043] On the other hand, the excitation spectrum 1 of Sample B is measured, acting as the monitor of the 440nm luminescence. Moreover, the emission spectrum 1 of B is what measured 255nm as an excitation light, and the emission spectrum 2 of B measures 335nm as an excitation light.

[0044] Although excitation and the emission spectrum of Sample A differ from both the spectrums of Sample B, when it often observes, there are two peaks in each excitation spectrum.



Moreover, both samples are similar if it takes into consideration that a broadcloth emission spectrum peak exists like 350-600nm. In addition, the absorption of parent material whose fluorescent glass has the 255nm peak of an excitation spectrum, and the peak which is 335nm belong as own absorption of Cr<sup>3+</sup> ion, respectively.

[0045] The example raw material powder which doped example 4Mn<sup>2+</sup> was mixed by the following composition, this mixed-sample powder was wrapped in the molybdenum foil, heating fusion was carried out for 2 hours, it quenched further, and the fluorescent glass was obtained [ in / the bottom of nitrogen-gas-atmosphere mind, and 1700 degrees C / using a high-frequency-heating furnace ]. In addition, in order to examine the homogeneity of the obtained sample about the fluorescent glass which carried out activation of Mn<sup>2+</sup>, respectively, two kinds were produced, respectively.

[0046] ((A) Sample)

CaCO<sub>3</sub> : Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> : AlN : MnCO<sub>3</sub> = 29.9 : 2.8 : 33.2 : 33.1 : 1.0 (N:5wt%) (Mn:1.0%)

((B) Sample)

CaCO<sub>3</sub> : Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> : AlN : MnCO<sub>3</sub> = 29.9 : 2.8 : 33.2 : 33.1 : 1.0 (N:5wt%) (Mn:1.0%)

[0047] Excitation and the emission spectrum of the calcium 1 aluminum-Si-O-N system oxy-nitride glass which doped Mn<sup>2+</sup> ion to drawing 5 <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000007](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000007)> are shown. The oxy-nitride glass which doped Mn<sup>2+</sup> from comparison of the excitation and the emission spectrum of the sample A in drawing 5 <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000007](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D125%26N0552%3D9%26N0553%3D000007)> and Sample B is uniform.

[0048]

[Effect of the Invention] The position of an excitation spectrum moves to a long wavelength side remarkably as compared with oxide glass, and if the fluorescent substance of this invention is combined with this fluorescent substance when InGaN system blue Light Emitting Diode is made into the excitation light source, since an absorption peak serves as the maximum in the luminescence peak neighborhood (450-520nm) of blue Light Emitting Diode and a peak width also becomes large further, it is excited efficiently and can realize brighter white Light Emitting Diode. Moreover, if structure can fill even a loose part and a reaction condition unlike a crystal like an oxy-nitride, glass can change freely the ratio of O and N in oxy-nitride glass, and can attain easily multiple color-ization of the fluorescent substance by change of N content.

[Brief Description of the Drawings]

[Drawing 1] <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000003](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000003)> Drawing 1 <<http://www4.ipdl.jpo.go.jp/cgi->

[bin/tran\\_web\\_cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000003](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000003)> is the graph of the excitation and the fluorescence spectrum which shows N content dependency of the oxy-nitride glass which doped Eu of this invention.

[Drawing 2] <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web\\_cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000004](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000004)> Drawing 2 <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web\\_cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000004](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000004)> is the graph of the excitation and the fluorescence spectrum which shows the amount dependency of Eu(s) of the oxy-nitride glass which doped Eu of this invention.

[Drawing 3] <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web\\_cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000005](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000005)> Drawing 3 <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web\\_cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000005](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000005)> is the graph of the excitation and the fluorescence spectrum of the oxy-nitride glass which doped Ce of this invention.

[Drawing 4] <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web\\_cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000006](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000006)> Drawing 4 <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web\\_cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000006](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000006)> is the graph of the excitation and the fluorescence spectrum of the oxy-nitride glass which doped Cr of this invention.

[Drawing 5] <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web\\_cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000007](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000007)> Drawing 5 <[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web\\_cgi\\_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000007](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web_cgi_ejje?u=http%3A%2F%2Fwww6.ipdl.jpo.go.jp%2FTokujitu%2Ftjitemdrw.ipdl%3FN0000%3D237%26N0500%3D1E%5FN%2F%3B%3E%3C%3D%3E%3B%3E9%3D%2F%2F%2F%26N0001%3D134%26N0552%3D9%26N0553%3D000007)> is the graph of the excitation and the fluorescence spectrum of the oxy-nitride glass which doped Mn of this invention.

## CLAIMS

[Claim(s)]

[Claim 1]  $\text{CaCO}_3$  is converted into  $\text{CaO}$  by mol % display, and it is :20-50-mol % and aluminum  $2\text{O}_3$ . : Fluorescent substance with which the sum total of five components made parent material the 100-mol oxy-nitride glass with which it becomes % at 0-30-mol % and  $\text{SiO}_2$ :25-60-mol % and  $\text{AlN}$ :5-50-mol % and rare earth oxide or transition-metals oxide:0.1-20-mol %.

[Claim 2] The fluorescent substance which made parent material the oxy-nitride glass according to claim 1 characterized by a nitrogen content being less than [ 15wt% ].

[Claim 3] The fluorescent substance which made parent material the oxy-nitride glass according to claim 1 characterized by containing as a coactivator by 0.1-10-mol % of a content in a fluorescent glass by using other rare-earth-elements ion used as the sensitizer other than a rare earth oxide ion according to claim 1 as a rare earth oxide.

[Claim 4] White light emitting diode which uses InGaN system blue light emitting diode as the light source, and is characterized by using the fluorescent substance indicated by a claim 1 or any one of the 3.

[Translation done.]

1. . . . .  
2. . . . .  
3. . . . .